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(71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).

(72) Inventor: HOLMAN, Eric, L.; 340 N. Clark Street, West Salem, WI 54669 (US).

(74) Agents: CRISS, Roger, H. et al.; AlliedSignal Inc., Law Dept. (Amy Olinger), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).

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(54) Title: INTERMEDIATE LAYER TO IMPROVE PEEL STRENGTH OF COPPER FOILS

(57) Abstract

A method is disclosed for providing an improved adherence, or peel strength, between copper foil and a circuit board laminate having low dielectric and high glass transition temperature, through the use of an intermediate organic resin compound. Epoxy and phenoxy resins having average molecular weight in excess of 4500 are preferred to achieve necessary increases in peel strength for low dielectric circuit board laminate materials.

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INTERMEDIATE LAYER TO IMPROVE PEEL STRENGTH OF COPPER FOILS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from provisional patent application Serial No. 60/046,598 filed May 15, 1997.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

BACKGROUND OF THE INVENTION

In the design and implementation of electronic circuitry, there is a strong incentive to make the circuit layouts as dense as possible. In the interests of making circuit designs more dense, it is desirable that the circuitry board has a low dielectric constant (Dk) and a high glass transition temperature (Tg). However, it has been observed that the peel strength value for a copper-clad laminate can be significantly reduced when a low Dk, high Tg resin system is employed, relative to the peel strengths obtained when a standard resin system is employed. Peel strength refers to the strength of adhesion of coated copper layers to a circuit board substrate and high peel strength is generally desirable. Peel strength may be even more severely reduced when low or very low profile copper foils are employed. However, low or very low profile copper foils are critical to the success of circuit board laminates for use in very dense circuit designs.

Typically, when attaching copper foils to fiberglass impregnated epoxy resin laminates for circuit board construction, no intermediate adhesive layer is required. Usually, if the rougher side of the copper foil is placed in contact with the uncured resin laminate, and heat is applied, the mechanical interaction between the foil an the resin of the laminate is sufficient to hold the foil to the laminate. However, as the material of the board is altered, particularly

as nonpolar materials are added to the board to increase its dielectric properties, this mechanical bond can become insufficient. This problem is made worse by the use of so-called low or very low profile copper foils which are thinner and which therefore also tend to have smaller surface irregularities.

Studies conducted using both present commercial products and products that are under development have shown that few foil and low Dk boards are currently capable of meeting the requirements of new military specifications (MIL-S-13949/4D) for peel strength in dense circuitry after thermal stress conditioning. One specification requires minimum peel strength of 8.0 pounds per linear inch (pli).

One form of adhesive that is sometimes used to and in bonding of resin to foil is to first coat the foil with a layer of uncured liquid resin itself which is intended to assist an integrating the foil to the laminate. Often such upper foils are coated with silane, which is believed to aid adhesion. U.S. Patents 5,525,433 and 5,629,433 describe some multifunctional epoxy compounds which can be used to attach foils to a laminate pre-preg.

There exists a need for a method of making a copper-clad laminate having an increased peel strength relative to prior art laminates.

BRIEF SUMMARY OF THE INVENTION

The present invention is a method of manufacturing a copper-clad laminate having enhanced peel strength comprising the step of applying an organic resin coating selected from the group consisting of high molecular weight epoxy or phenoxy resins or combinations thereof to a surface of a copper foil and laminating the copper foil to a low Dk laminate.

The present invention is also a copper-clad laminate made by applying an organic resin coating to a surface of a copper foil and laminating the copper foil to a laminate, the organic resin selected from the group consisting of epoxy or phenoxy resins or combinations thereof.

It is an object of the present invention to provide a copper-clad laminate having a low dielectric constant, a high glass transition temperature, and a peel strength that meets industry standards.

Other objects, advantages, and features of the present invention will become apparent after review of the specification and drawings.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

Fig. 1 is a plot of peel values (pli) of copper-clad laminate after thermal stress conditioning as a function of the number average molecular weight (Mn) of the organic resin coating applied to the copper foil prior to lamination.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a method of manufacturing a low Dk, high Tg copper-clad laminate having enhanced peel strength comprising the step of applying a high molecular weight organic resin coating to a surface of the copper foil prior to lamination. The present invention is also directed to the laminate materials and circuit boards made using this method.

The organic resin coating for use within the present invention is preferably an uncured epoxy or phenoxy resin, or combinations thereof, having an average molecular weight greater than 4500. It has been found that high molecular weight epoxy and phenoxy compounds provided greater peel strength for low Dk and high Tg boards than other adhesives of lower molecular weight.

By "enhanced peel strength" it is meant that the peel strength after thermal stress conditioning exceeds the peel strength of a control laminate in which lamination occurs without applying an organic resin coating to a surface of the copper foil prior to lamination. Preferably, the peel strength is enhanced at least about 100% greater than the peel strength of a comparable laminate lacking the organic resin coating on the copper film. Determining the peel strength of a laminate by standard methods is well within the ability of one of

ordinary skill in the art.

As demonstrated in the examples below, peel strength is affected by numerous factors, including the dielectric constant (Dk) and glass transition temperature (Tg) of the laminate, the profile of the copper foil, the number average molecular weight (Mn) of the organic resin coating on the copper foil, and the thickness of the organic resin coating applied. For a particular laminate and foil, there exists a direct linear relationship between peel strength and Mn of the organic resin employed (Fig 1). For example, when a laminate product having a low Dk and a high Tg (e.g., AlliedSignal Laminate Systems product FR408) and a very low profile copper foil (e.g. AlliedSignal Oak-Mitsui 1 oz. MLS) are laminated together, an organic resin having an Mn of at least about 4500 is required in order to obtain a peel strength of about 8.0 pli. However, it is well within the ability of one of ordinary skill in the art to determine the minimum Mn required using the guidance provided herein.

By a laminate having a low Dk and a high Tg, it is meant a laminate having a Dk of less than about 4.5 and a Tg of greater than about 170°C. The Dk value of the fiberglass and the impregnating resin are different and thus the Dk depends on the resin content of the laminate. Low Dk laminates generally have Dk values between 2.5 and 4.5 and preferably between 3.0 and 4.0. These values may be measured using a Hewlett Packard Materials/Impedance Analyzer, Model 4291A, operating at 100 MH_z.

The peel strength increases with the treatment thickness of the organic resin applied to the copper foil prior to lamination. A copper coated laminate having a peel strength of about 8.0 pli when a FR408 laminate, or its equivalent, is laminated to a copper foil equivalent to CircuitFoils NTTW-HTE-1/2 oz using a treatment of a 0.1 mil coating of organic resin as specified here. The minimum treatment thickness required to achieve a particular peel strength may vary depending on the laminate, the copper foil, and the organic resin. The preferred range of thickness of this organic resin is between

.05 mils and .50 mils, with the most preferred being .08 to .16 mils. However, it is well within the ability of one of ordinary skill in the art to determine the minimum treatment thickness required for a particular selection of starting materials.

Although the copper-clad laminates described in the examples were prepared by applying the organic resin to the copper foil prior to lamination, it is anticipated that the organic resin could be applied to the laminate prior to lamination of the copper foil. It is also specifically envisioned that copper foils can be pre-treated with the organic resin and stored until needed for lamination. What is important is simply the use of the organic resin to bind the copper foil to the laminate material.

The examples below describe a method for manufacturing a copper clad laminate having a high peel strength using commercial epoxy or phenoxy products obtained from Phenoxy Specialties or Ciba-Geigy as the organic resin. It is expected that any epoxy or phenoxy resin could be employed in the practice of the present invention, provided that the resin has a sufficiently high number average molecular number. It is reasonably anticipated that any polymer that has a sufficiently high molecular weight and which is reactive toward epoxy resins or epoxy curatives could be used in the practice of the present invention.

The nonlimiting examples that follow are intended to be purely illustrative.

Effect of organic resin adhesive on peel strength of copper-clad laminate

To determine whether an organic resin coating applied to the copper foil surface prior to lamination enhances copper adhesion to the FR408 laminate product, the following experiment was conducted using the FR408 laminate product. A copper-clad laminate was made by laminating, 2 plies of 7628-(41% resin content) (.014 inches) and AlliedSignal Oak-Mitsui 1 oz. MLS (reverse-treated, coated, very low profile) copper foil

using an organic resin, PAPHEN Phenoxy solution PKHS-40 (Phenoxy Specialties, Inc.) was diluted to 8% solids with MEK solvent and brush applied to the copper foil prior to lamination to the FR408 laminate product. As a control, the laminate and copper foil were laminated without the resin. Peel strength measurements after thermal conditioning were made according to standard methods known to one of ordinary skill in the art. The results of this experiment are shown in Table 1.

Table 1

Peel Strength Results

Sample	Peel Strength (pli)	Tg	Dk
Untreated control	2.3	182	4.1
Treated Sample 1	7.0	182	4.1
Treated Sample 2	6.9	177	4.1

Effect of molecular number weight (Mn) of organic resin on peel strength

Additional epoxy-phenoxy resin products were evaluated for peel strength enhancement. The products listed below were selected because of their varied Number Molecular Weight, Mn. A copper foil (standard HTE-1 oz. foil) enhanced with a resin coating of these products were evaluated for copper peel adhesion to the FR408 laminate product. The results are shown in Table 2.

Table 2

Peel Strength Results

Sample	Organic Resin	Supplier	Mn	Peel, Thermal Stress, pli
control				6.0
A	Araldite PZ 3901	Ciba-Geigy	1062	6.0
B	Araldite PZ 3907	Ciba-Geigy	3948	7.1
C	PKHW-34	Phenoxy Specialties	5500	9.5
D	Araldite GZ488 N40US	Ciba-Geigy	13378	11.6
E	PKHW-35	Phenoxy Specialties	13000	12.0
F	PKHS-40	Phenoxy Specialties	13000	12.2

A plot of Mn versus peel strength for these resins shows a positive linear relationship between the Mn of the organic

resin and peel strength (Fig. 1). The plot indicates that when employing the FR408 laminate product or an equivalent and a standard HTE-1 oz. foil, the resin must have a Mn of at least about 4500 to meet the MIL-S-13949 specification of 8.0 pli.

Effect of treatment thickness on peel strength

PKHS-40 phenoxy resin solution was diluted to various levels of solids content and brush applied to produce different dry film thickness levels on the copper foil substrate (CircuitFoils standard profile NTTW-HTE-1/2 oz.) to evaluate the effect of treatment thickness on peel strength of copper-clad FR408 laminates. The treatment thickness was determined using a Veeco MP-900 B-Backscatter thickness measuring unit. The results indicate a minimum thickness requirement at or about 0.1 mils in order to obtain significant improvement in peel strength (Table 3). The preferred range is 0.5-.5 mils, thus minimizing any increase in thickness caused by the adhesive while supplying adequate strength, with the most preferred thickness being .08 to .16 mils.

Table 3

Impact of Treatment Thickness

Level	Treatment Thickness, mils	Peel strength (pli) Treated	control
1	0.05	4.8	4.2
2	0.12	8.2	3.9
3	0.14	8.2	4.1
4	0.19	8.4	3.8
5	0.20	8.4	3.7

The best practice to date for manufacturing the treated foil product on a large scale consists of reverse roll coating foils as supplied from the foil manufacturer. However, any process method of coating may be employed as long as the resultant coating thickness is in the desired range.

A experiment was conducted using a variety of low and very low profile copper foils to determine peel strength enhancements using the PKHS-40 phenoxy resin treatment. The results of this experiment are shown in Table 4.

Table 4

Peel Strength Results

Foil Vendor	FoilProduct	Tooth Profile	Peel strength (pli) Treated	control
Oak-Mitsui	TOBIII-ML- 1/2 oz.	low	9.2	4.6
Oak-Mitsui	TOBIII-ML- 3/8 oz.	low	7.8	2.9
Oak-Mitsui	MLS- 1/2 oz.	very low	8.0	3.5
Oak-Mitsui	MLS- 1 oz.	very low	9.1	3.7
Gould	JTCS- 1/2 oz.	low	8.6	3.0

It is understood that the present invention is not to be limited to the particular embodiments and examples illustrated above but encompasses all such modifications and variations thereof as come within the scope of the following claims.

CLAIMS

What is claimed is:

1. A method of making a low Dk, high Tg copper-clad laminate having enhanced peel strength comprising the steps of:

(a) applying an organic resin solution of an organic resin having an average molecular weight in excess of 4500 to a surface of one of a copper foil and a fiberglass impregnated resin laminate; and

(b) laminating the copper foil to the laminate.

2. The method of claim 1, wherein the organic resin is selected from the group consisting of an epoxy or a phenoxy.

3. The method of claim 1 wherein the copper foil is low profile copper foil.

4. The method of claim 1 wherein the copper foil-very low profile copper foil.

5. The method of claim 1 wherein the Dk of the laminate is less than about 4.5.

6. The method of claim 5 wherein the Dk of the laminate is between 2.0 and 4.0.

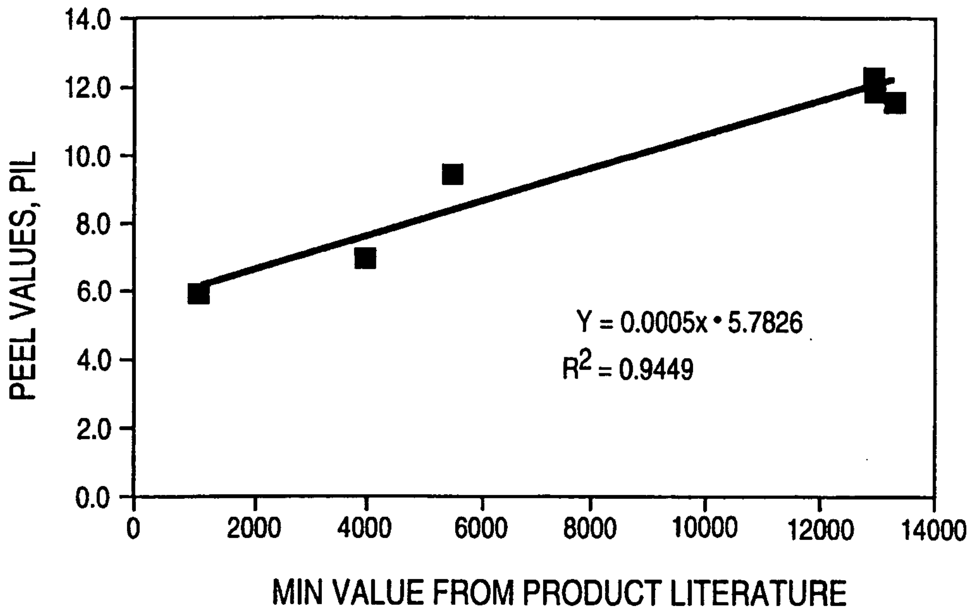
7. The method of claim 1 wherein the Tg is above about 170°C.

8. A circuit board stock material comprising a printed circuit board laminate and a copper foil, the copper foil bound to the laminate by an organic resin selected from the group consisting of epoxy and phenoxy resins and having an average molecular weight in excess of 4500.

9. The laminate of claim 8, wherein the laminate has a Dk of less than about 4.5, and wherein the laminate comprises a low profile copper foil or a very low profile copper foil.

10. The laminate of claim 8, wherein the laminate has a peel strength of at least about 8.0 pli.

FIG. 1


14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
PEEL VALUES, PIL
0
2000
4000
6000
8000
10000
12000
14000
MIN VALUE FROM PRODUCT LITERATURE
Y = 0.0005x • 5.7826
R2 = 0.9449

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/09551

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H05K3/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 486 655 A (ARIKE SHIGEHARU ET AL) 23 January 1996 (1996-01-23) column 7, line 4 - line 16	1-10
A	EP 0 227 002 A (KOLLMORGEN TECH CORP) 1 July 1987 (1987-07-01) claim 1	1
A	US 3 873 637 A (NAITO KEIICHI ET AL) 25 March 1975 (1975-03-25) claim 1	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 August 1999	13/08/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/09551

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